

Supporting Information

Steric Effect of α - and β -Substituted Anthraquinone Units on High Performance Polymeric Memory Devices

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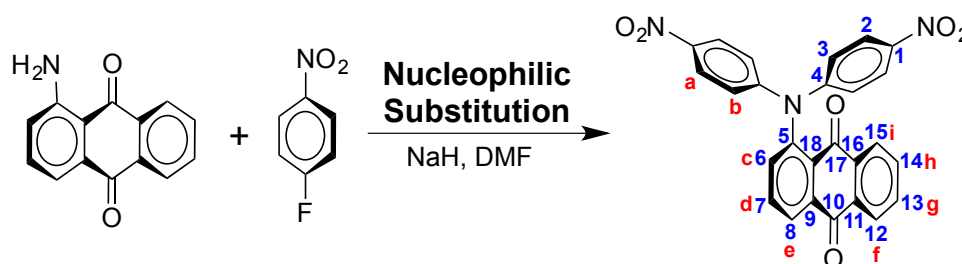
List of Contents for Supplementary Material:

Experimental Section	<u>SI-2</u>
Figure S1. (a) ¹ H and (b) ¹³ C NMR spectra of dinitro α-dinitro in DMSO- <i>d</i> ₆	<u>SI-8</u>
Figure S2. 2D (a) H-H COSY and (b) C-H HSQC NMR spectra of α-dinitro	<u>SI-9</u>
Figure S3. (a) ¹ H and (b) ¹³ C NMR spectra of α-diamine in DMSO- <i>d</i> ₆	<u>SI-10</u>
Figure S4. 2D (a) H-H COSY and (b) C-H HSQC NMR spectra of α-diamine	<u>SI-11</u>
Figure S5. ¹ H NMR spectrum of polyimide α-6FPI in DMSO- <i>d</i> ₆	<u>SI-12</u>
Figure S6. ¹ H NMR spectrum of polyamide α-TPA in DMSO- <i>d</i> ₆	<u>SI-13</u>
Figure S7. TGA traces of polyimides and polyamides.....	<u>SI-14</u>
Figure S8. TMA traces of polyimides and polyamides.....	<u>SI-15</u>
Figure S9. Absorption spectra of (a) polyimide and (b) polyamide thin films.	<u>SI-16</u>
Figure S10. Calculated molecular orbitals and energy levels of polyimides	<u>SI-17</u>
Figure S11. Calculated molecular orbitals and energy levels of polyamides.....	<u>SI-18</u>
Figure S12. <i>In situ</i> UV-visible spectra of the polymeric memory devices (a) α-6FPI and (b) α-6FPA	<u>SI-19</u>
Table S1. Inherent Viscosity and Molecular Weights of Polymers.....	<u>SI-20</u>
Table S2. Solubility Behaviors of Polymers.....	<u>SI-21</u>
Table S3. Thermal Properties of Polymers.....	<u>SI-22</u>

Experimental Section

Materials: Polymers β -DSPI and β -TPA were synthesized according to a previously reported procedure.¹⁶ 2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (Chriskev) was purified by vacuum sublimation. Oxydiphthalicanhydride (Chriskev) and 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride were purified by recrystallization from acetic anhydride. Tetrabutylammonium perchlorate (TBAP) (Acros) was recrystallized twice by ethyl acetate in a nitrogen atmosphere and then dried *in vacuo* prior to use. All other reagents were used as received from commercial sources.

Monomer Synthesis:

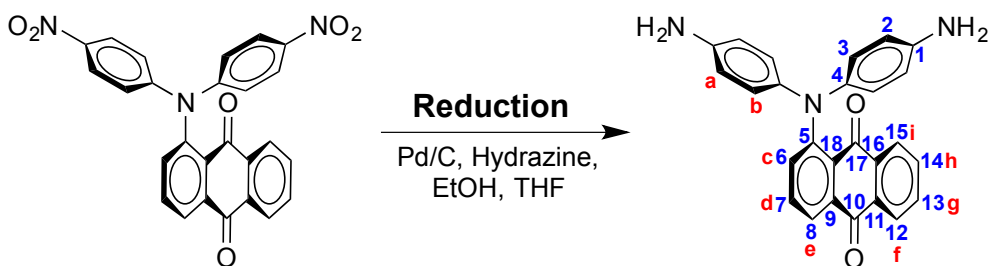


1-(bis(4-nitrophenyl)amino)anthracene-9,10-dione (α -dinitro)

A mixture of 1.32 g (0.053mol) of sodium hydride in 50 mL of DMF was stirred at room temperature. To the mixture, 5.58 g (0.025mol) of 1-aminoanthraquinone and 7.41 g (0.053mol) of 4-fluoronitrobenzene were added in sequence. The mixture was heated with stirring at 150 °C for 72 h under nitrogen. The mixture was poured slowly into 500 mL of stirred water, and the precipitated red powder was collected by filtered and washed thoroughly with methanol. The product was filtered and recrystallized from DMF to give 6.63g (57% in yield) of red crystal with a mp of 186-188 °C (by Melting Point System at a scan rate of 5 °C /min).

IR (KBr): 1580 and 1308 cm^{-1} ($-\text{NO}_2$ asymmetric and symmetric stretch). ^1H NMR (600 MHz, $\text{DMSO}-d_6$, δ , ppm): 7.25 (d, 4H, H_b), 7.82-7.85 (m, 2H, H_c+H_h), 7.89 (t, 1H, H_g), 7.93(d, 1H,

H_i), 8.07 (t, 1H, H_d), 8.15 (d, 4H, H_a), 8.18 (d, 1H, H_f), 8.37(d, 1H, H_e). ¹³C NMR (150 MHz, DMSO-*d*₆, δ, ppm): 121.54, 125.15, 126.32, 126.59, 127.36, 129.31, 132.11, 133.69, 134.24, 134.65, 136.20, 136.23, 138.17, 141.78, 142.81, 150.83, 180.77, 182.02. Anal. Calcd (%) for C₂₆H₁₅N₃O₆ (465.41): C, 67.10; H, 3.25; N, 9.03. Found: C, 67.41; H, 3.60 ; N, 9.42.



1-(bis(4-aminophenyl)amino)anthracene-9,10-dione (α-diamine)

In 100-mL three-neck round-bottomed flask equipped with a stirring bar under nitrogen atmosphere, 1.50 g (3.00 mmol) of dinitro compound **α-dinitro** and 0.15 g of 10 % Pd/C were dispersed in 5 mL of ethanol and 20 mL THF. The suspension solution was heat to reflux, and 2.0 mL of hydrazine monohydrate was added slowly to the mixture. After a further 48 h of reflux, the solution was filtered to remove Pd/C, and the filtrate was cooled under nitrogen atmosphere. The precipitated product was collected by filtration and dried *in vacuo* at 100 °C to give 0.85 g (70% in yield) of dark-green crystal with a mp of 304-305 °C (by Melting Point System at a scan rate of 5 °C /min).

IR (KBr): 3372, 3464 cm⁻¹ (primary and secondary N-H stretch). ¹H NMR (600 MHz, DMSO-*d*₆, δ, ppm): 4.87(s, 4H, -NH₂), 6.45 (d, 4H, H_a), 6.64 (d, 4H, H_b), 7.33 (d, 1H, H_c), 7.61 (t, 1H, H_d), 7.74-7.79 (m, 4H, H_e+H_g+H_h+H_i), 8.06-8.08 (m, 1H, H_f). ¹³C NMR (150 MHz, DMSO-*d*₆, δ, ppm): 114.56, 120.36, 124.28, 124.48, 125.97, 126.17, 131.79, 132.65, 133.04, 133.59, 134.37, 134.85, 135.51, 137.71, 144.68, 149.28, 179.24, 182.66. Anal. Calcd (%) for C₂₆H₁₉N₃O₂ (405.45): C, 77.02 ; H, 4.72 ; N, 10.36. Found: C, 77.73; H, 4.52; N, 10.48.

Polymer Synthesis:

One-step High-temperature Polycondensation.

The synthesis of polyimide **α -6FPI** is used as an example to illustrate the general synthetic route used to produce the series of polyimides. The solution of **α -diamine** (1.0 mmol, 0.41 g), 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (1.0 mmol, 0.44 g), and 0.25 mL isoquinoline in 3 mL of *m*-cresol was mechanically stirred at room temperature in nitrogen atmosphere. After the solution was stirred for 24 h, it was heated to 200 °C for 15 h to imidization. After the imidization reaction, the mixture was allowed to cool to room temperature; the viscous solution then was poured slowly into 300 mL of methanol with stirring. The polymer that precipitated was collected by filtration, washed thoroughly with hot methanol, and dried under reduced pressure at 80 °C for 15 h. The FT-IR spectrum of **α -6FPI** (film) exhibited characteristic imide absorption bands at around 1781 (asymmetrical C=O), 1721 (symmetrical C=O) and 1675 cm⁻¹ (anthraquinone C=O). ¹H NMR (400 MHz, DMSO-*d*₆), δ (ppm): 8.17 (d, 1H, H_f), 8.08 (d, 3H, H_g+H_n+H_i), 7.87-7.91 (m, 4H, H_j+H_k), 7.76-7.72 (m, 3H, H_c+H_d+H_e), 7.67 (s, 2H, H_l), 7.26 (d, 2H, H_b), 7.09 (d, 2H, H_a). Anal. Calcd (%) for (C₄₅H₂₂F₆N₃O₆)_{*n*} (814)_{*n*}: C, 66.34 %; H, 2.72%; N, 5.16 %. Found: C, 66.18 %; H, 3.32 %; N, 5.19 %.

Direct Phosphorylation Polycondensation.

The synthesis of polyamide **α -CHPA** is used as an example to illustrate the polycondensation used to produce **α -CHPA** and **α -6FPA**. The polyamide **α -CHPA** was synthesized from diamine monomer **α -diamine** and *trans*-1,4-cyclohexanedicarboxylic acid. A mixture of 0.41 g (1.0 mmol) of **α -diamine**, 0.17 g (1.0 mmol) of *trans*-1,4-cyclohexanedicarboxylic acid,

0.12 g of calcium chloride, 1.0 mL of triphenyl phosphite, 0.5 mL of pyridine, and 2.0 mL of NMP was heated with stirring at 105 °C for 3 h. The obtained polymer solution was poured slowly into 300 mL of stirred methanol, fiber-like precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried under vacuum at 110 °C. Reprecipitations of the polymer by DMAc/methanol were carried out twice for further purification. The FT-IR spectrum of **α -CHPA** (film) exhibited characteristic absorption bands at 3288 cm⁻¹ (N-H stretch) and 1673 cm⁻¹ (amide carbonyl).

Low-temperature Solution Polycondensation.

The polyamide **α -TPA** was synthesized from diamine monomer **α -diamine** and terephthaloyl chloride (TPC). A solution of 0.41 g (1.0 mmol) of **α -diamine** in 3.0 mL of NMP was cooled with stirring at -20 °C on a ice/acetone bath. After 0.40 mL propylene oxide was added to the mixture, 0.20 g (1.0 mmol) of TPC was added into the mixture. The mixture was then stirred at -10 °C for 1 h then room temperature for 2 h. The resulting polymer solution was poured into 400 mL of methanol. The precipitated polymer was collected by filtration, and dried at 100 °C. Reprecipitations of the polymer by DMAc/methanol were carried out once for further purification. The yields of the polymers were 0.52 g (98%). The FT-IR spectrum of **α -TPA** (film) exhibited characteristic imide absorption bands at around 3309 cm⁻¹ (N-H stretch) and 1655 cm⁻¹ (amide carbonyl). ¹H NMR (400 MHz, DMSO-*d*₆), δ (ppm): 10.28 (s, 2H, -NH), 8.02-8.10 (m, 7H, H_e+H_f+H_g+H_h+H_i+H_j), 7.79-7.83 (m, 4H, H_b), 7.64 (m, 3H, H_c+H_k), 7.54 (s, 1H, H_d), 6.95 (d, 4H, H_a). Anal. Calcd (%) for (C₃₄H₂₁N₃O₄)_n (536)_n: C, 76.25 %; H, 3.95 %; N, 7.85 %. Found: C, 74.18 %; H, 4.33 %; N, 8.00 %.

Fabrication and Measurement of the Memory Device: The memory device was fabricated with the configuration of ITO/polymer/Al. The ITO glass used for memory device was

precleaned by ultrasonication with water, acetone, and isopropanol each for 15 min. A 250 μL DMAc solution of each polymer ($\sim 23\text{-}25$ mg/ml) was first filtered through 0.45 μm pore size of PTFE membrane syringe filter. Then, the 250 μL of filtered solution was spin-coated onto the ITO glass at a rotation rate of 1000 rpm for 60 s and kept at 100 $^{\circ}\text{C}$ for 10 mins under nitrogen. The film thickness was determined to be around 50 nm by alpha-step profilometer. Finally, a 300-nm-thick Al top electrode was thermally evaporated through the shadow mask (recorded device units of 0.5×0.5 mm² in size) at a pressure of 10^{-7} torr with a uniform depositing rate of 3-5 $\text{\AA}/\text{s}$. The electrical characterization of the memory device was performed by a Keithley 4200-SCS semiconductor parameter analyzer equipped with a Keithley 4205-PG2 arbitrary waveform pulse generator. ITO was used as the cathode (maintained as common), and Al was set as the anode during the voltage sweep.

Measurements: Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum 100 Model FT-IR spectrometer. Elemental analyses were run in a Heraeus VarioEL-III CHNS elemental analyzer. ¹H NMR spectra were measured on a Bruker AVANCE III HD 600 MHz NMR and Bruker DPX 400 MHz NMR using tetramethylsilane as the internal standard, and peak multiplicity was reported as follows: s, singlet; d, doublet. The inherent viscosities were determined at 0.5 g/dL concentration using Tamson TV-2000 viscometer at 30 $^{\circ}\text{C}$. Gel permeation chromatographic (GPC) analysis was carried out on a Waters chromatography unit interfaced with a Waters 2410 refractive index detector. Two Waters 5 μm Styragel HR-2 and HR-4 columns (7.8 mm I. D. \times 300 mm) were connected in series with NMP as the eluent at a flow rate of 0.5 ml/min at 40 $^{\circ}\text{C}$ and were calibrated with polystyrene standards. Thermogravimetric analysis (TGA) was conducted with a TA instrument Q50. Experiments were carried out on approximately 3-5 mg film samples heated in flowing nitrogen or air (flow rate = 20 cm³/min) at a heating rate of 20 $^{\circ}\text{C}/\text{min}$.

Thermal Mechanical Analyzer (TMA) was conducted with a TA instrument Q400. The TMA experiment was conducted from 40 to 450 °C at a scan rate of 10 °C / min with a penetration mode under an applied constant load of 5 mN. Cyclic voltammetry (CV) was performed with a Bioanalytical System Model CV-27 and conducted with the use of a three-electrode cell in which ITO (polymer films area about 0.5 cm x 1.2 cm) was used as a working electrode and a platinum wire as an auxiliary electrode at a scan rate of 50 mV/s against a Ag/AgCl reference electrode in anhydrous DMF and CH₃CN, using 0.1 M of TBAP as a supporting electrolyte in nitrogen atmosphere. All cell potentials were taken by using a homemade Ag/AgCl, KCl (sat.) reference electrode. The thickness of the polyimide thin films was measured by alpha-step profilometer (Kosaka Lab., Surfcoorder ET3000, Japan). The Gaussian 09 program package is used for theoretical calculation in this research. And the basic units of the polymers were optimized by means of the density functional theory (DFT) method at the B3LYP level of theory (Beckesstyle three-parameter density functional theory using the Lee-Yang-Parr correlation functional) with the 6-31G(d) basic set.

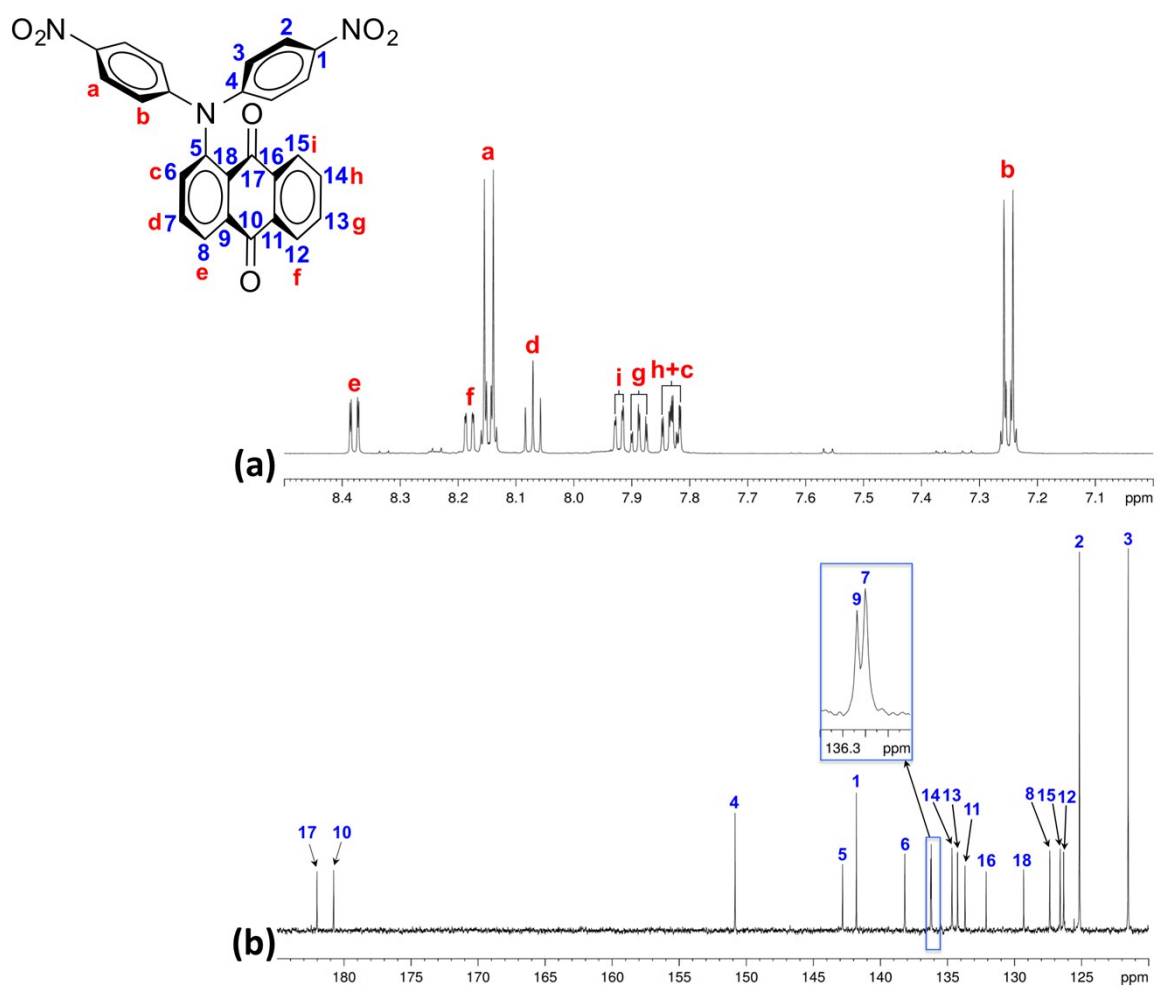


Figure S1. (a) ^1H and (b) ^{13}C NMR spectra of dinitro compound α -dinitro in $\text{DMSO-}d_6$.

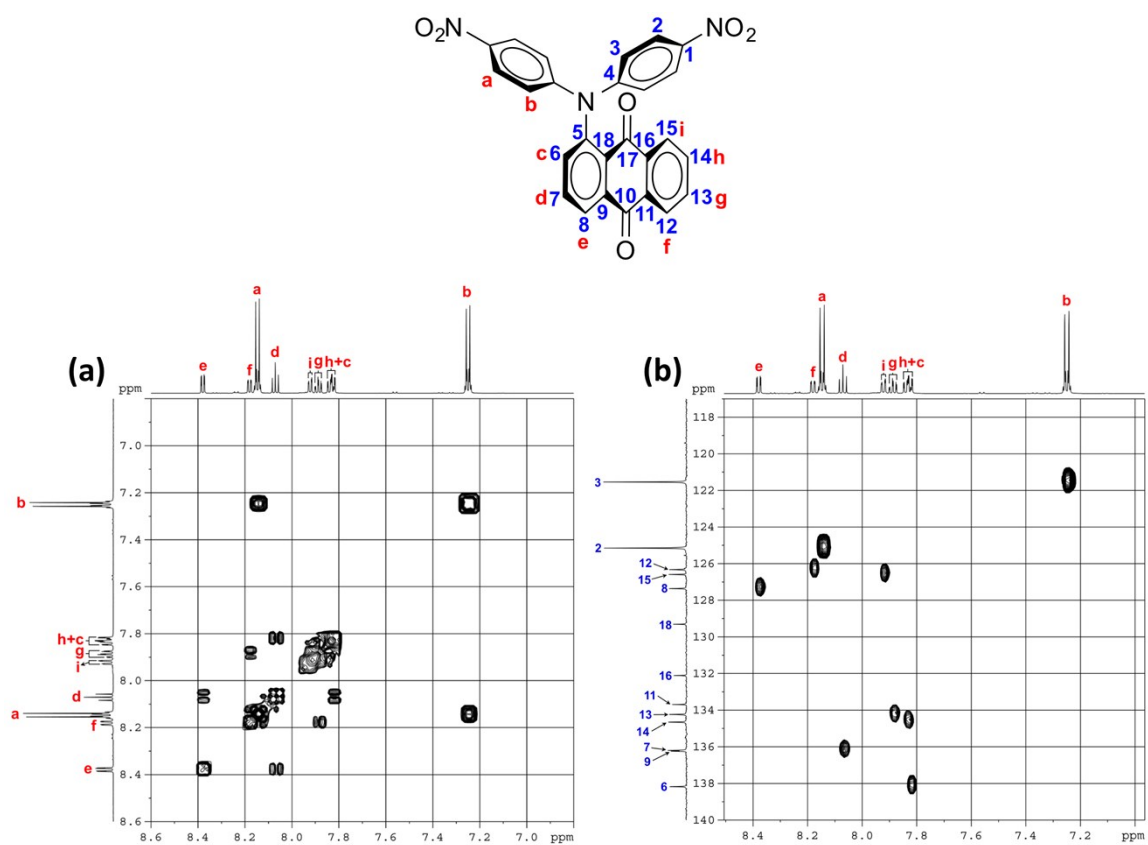


Figure S2. 2D (a) H-H COSY and (b) C-H HSQC NMR spectra of dinitro compound α -dinitro in DMSO- d_6 .

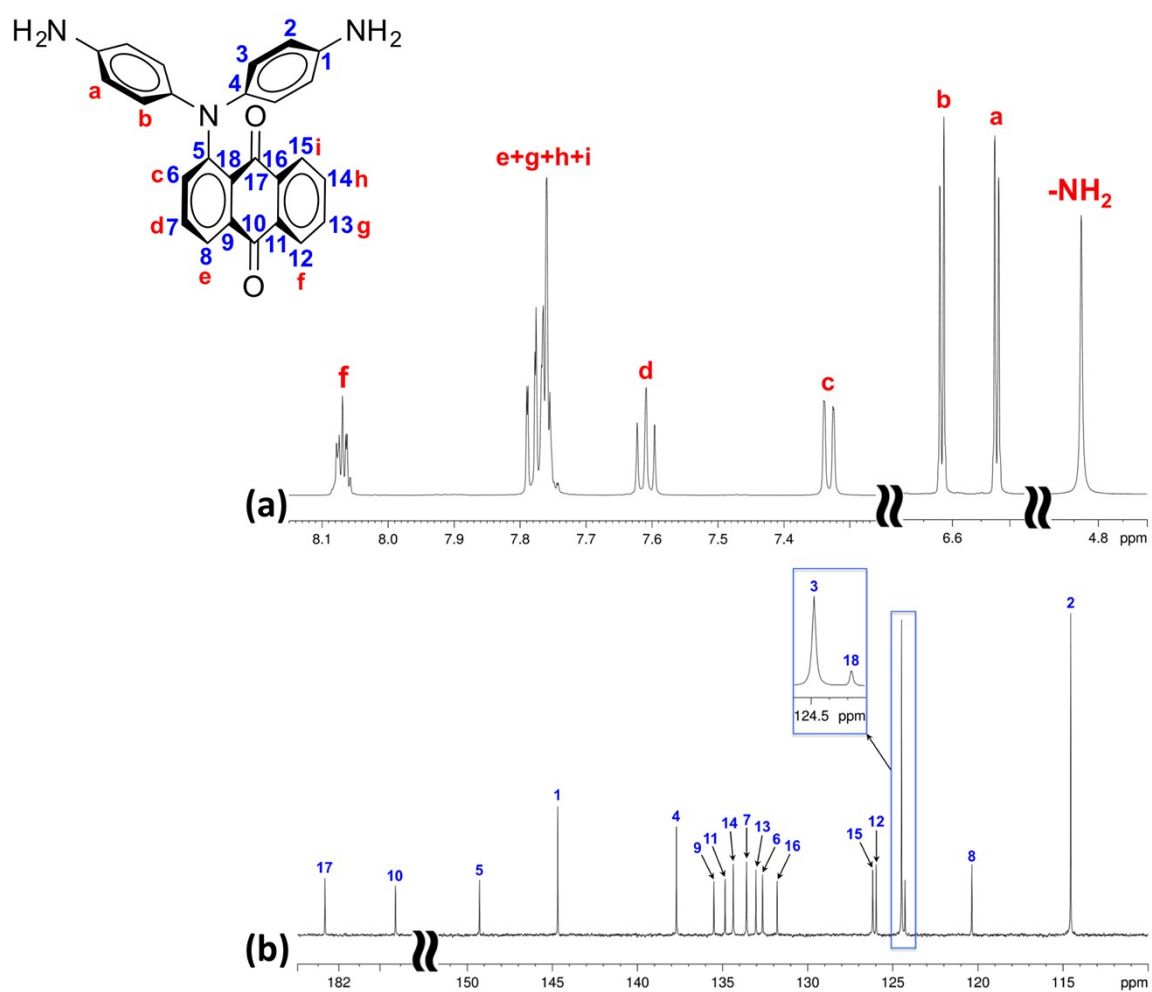


Figure S3. (a) ^1H and (b) ^{13}C NMR spectra of diamine monomer α -diamine in $\text{DMSO-}d_6$.

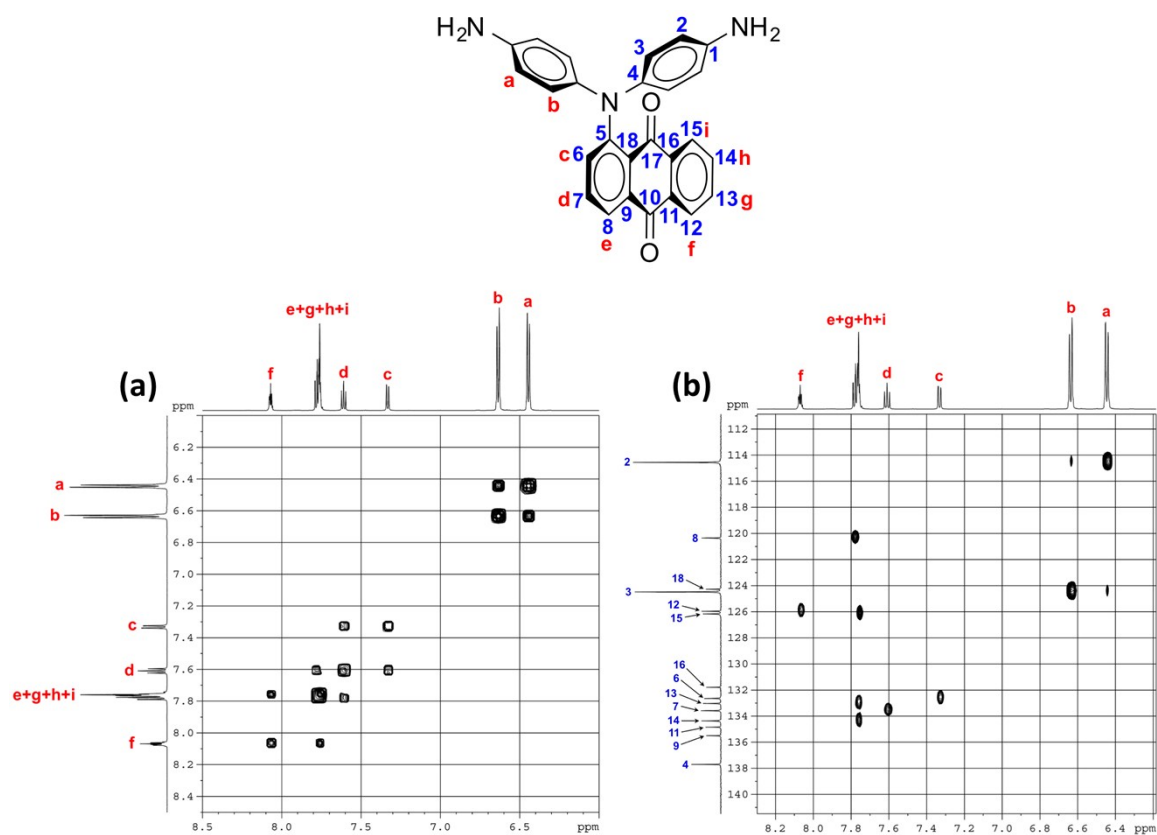


Figure S4. 2D (a) H-H COSY and (b) C-H HSQC NMR spectra of diamine monomer α -diamine in DMSO- d_6 .

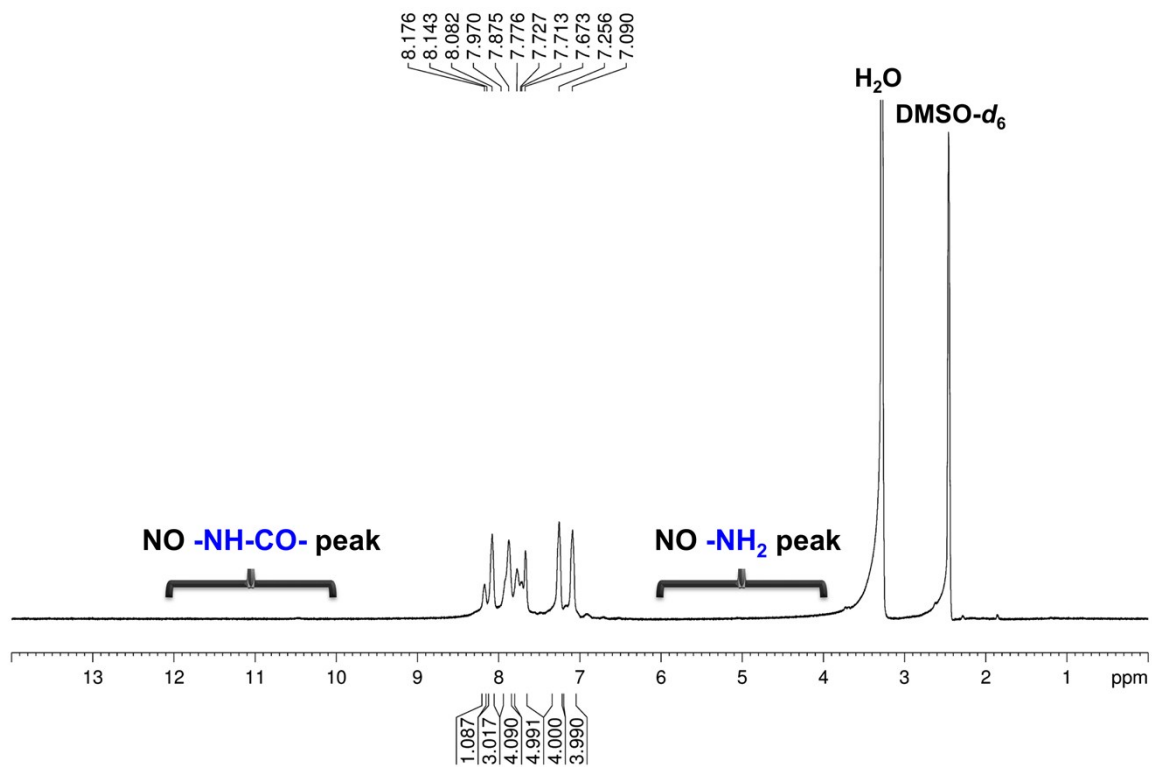


Figure S5. ^1H NMR spectrum of polyimide α -6FPI in $\text{DMSO-}d_6$.

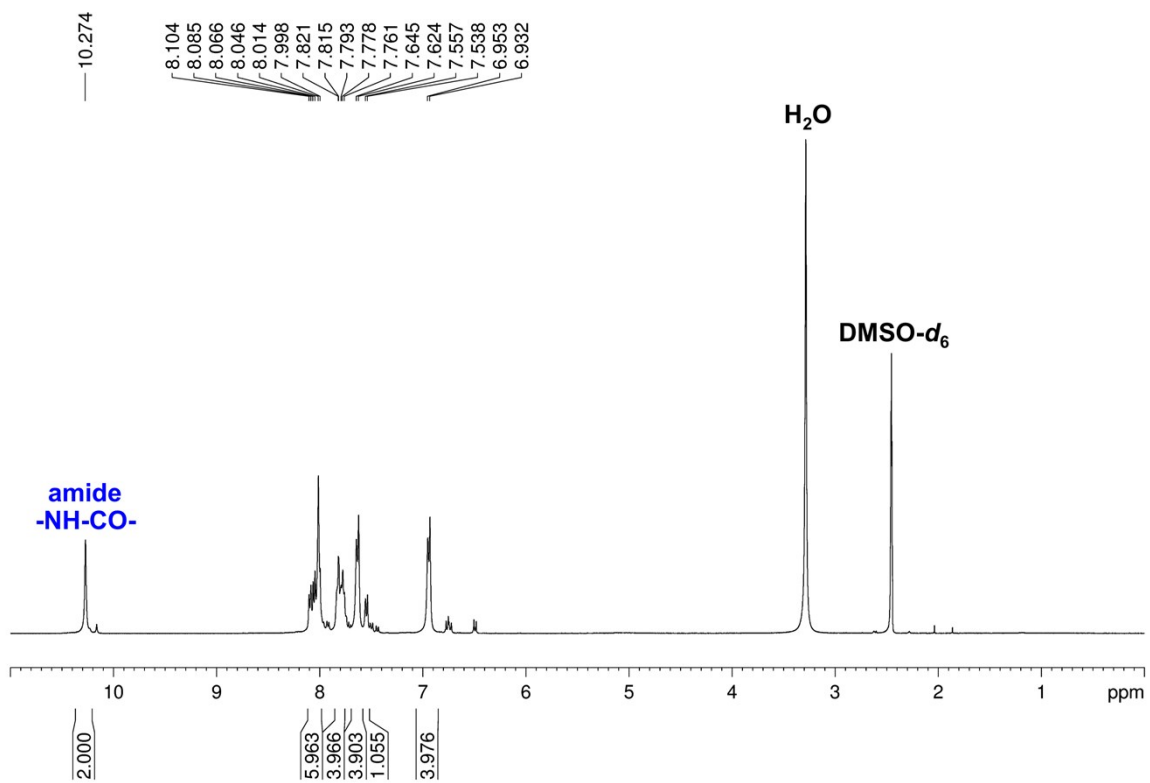


Figure S6. ¹H NMR spectrum of polyamide α -TPA in DMSO-*d*₆.

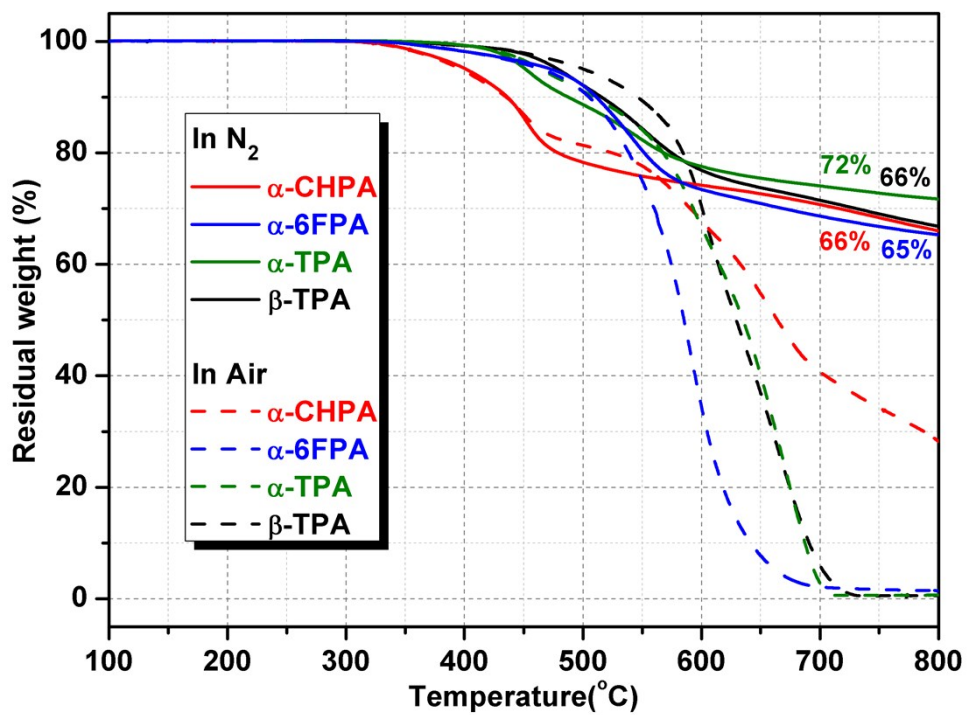
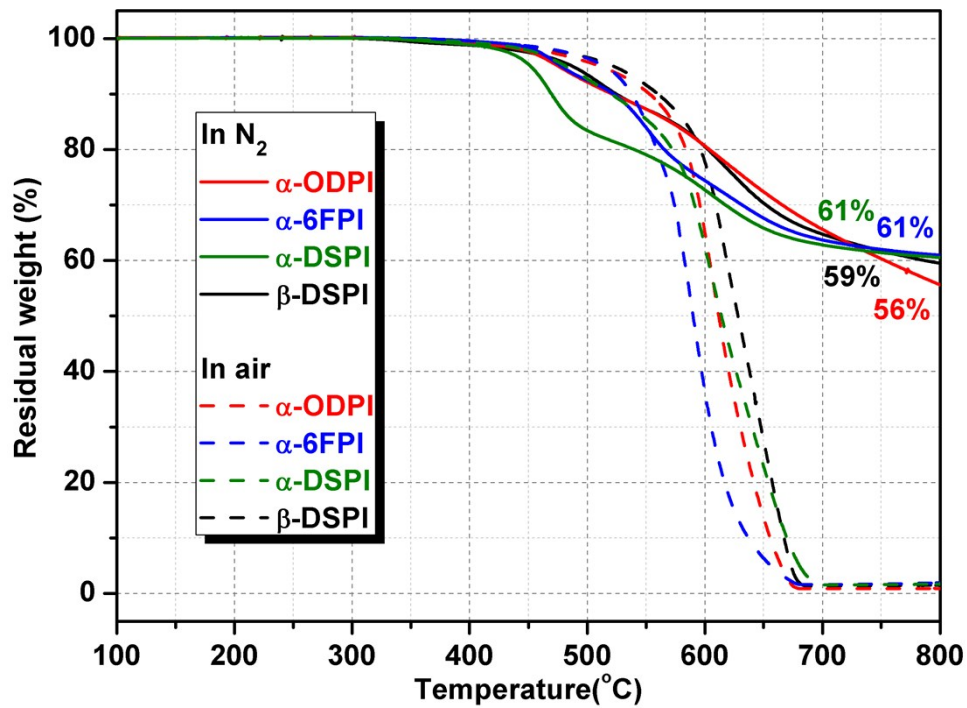


Figure S7. TGA traces of the polyimides and polyamides.

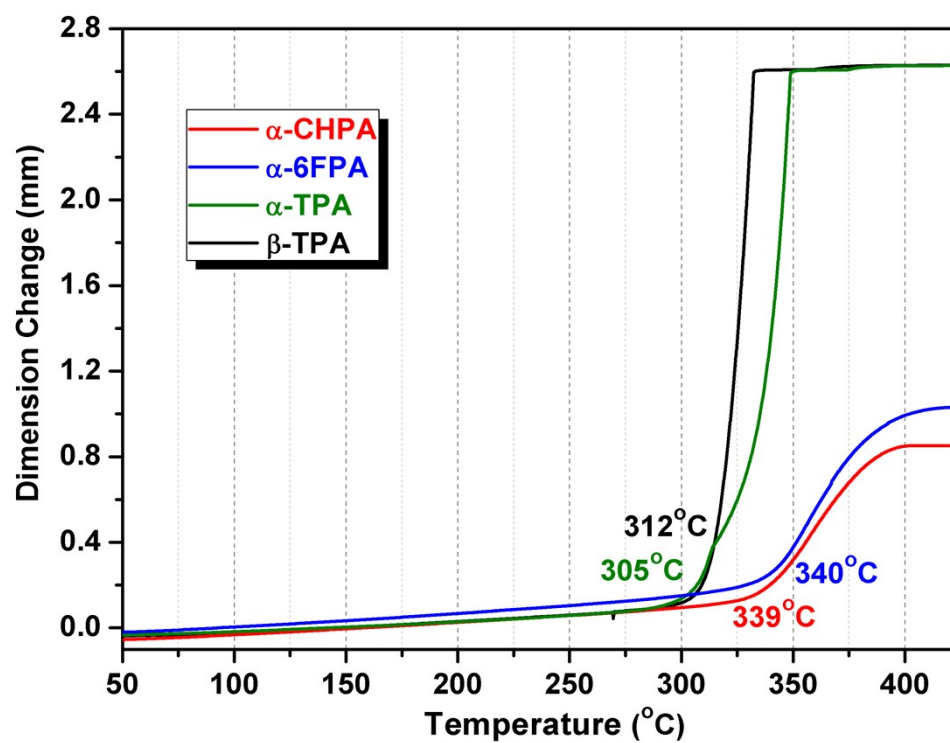
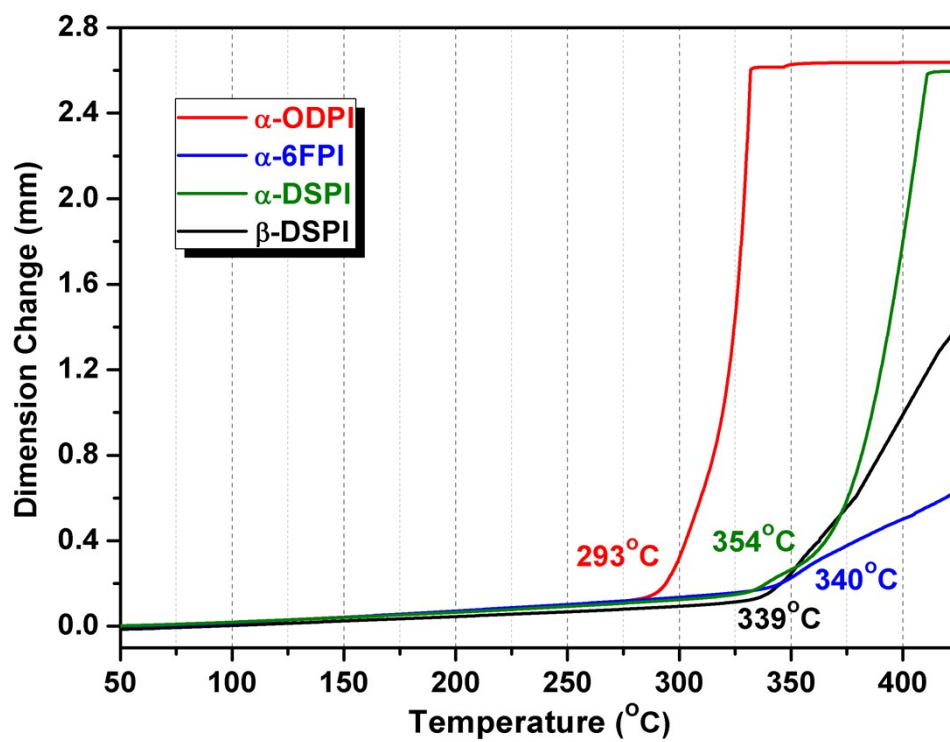


Figure S8. TMA traces of the polyimides and polyamides.

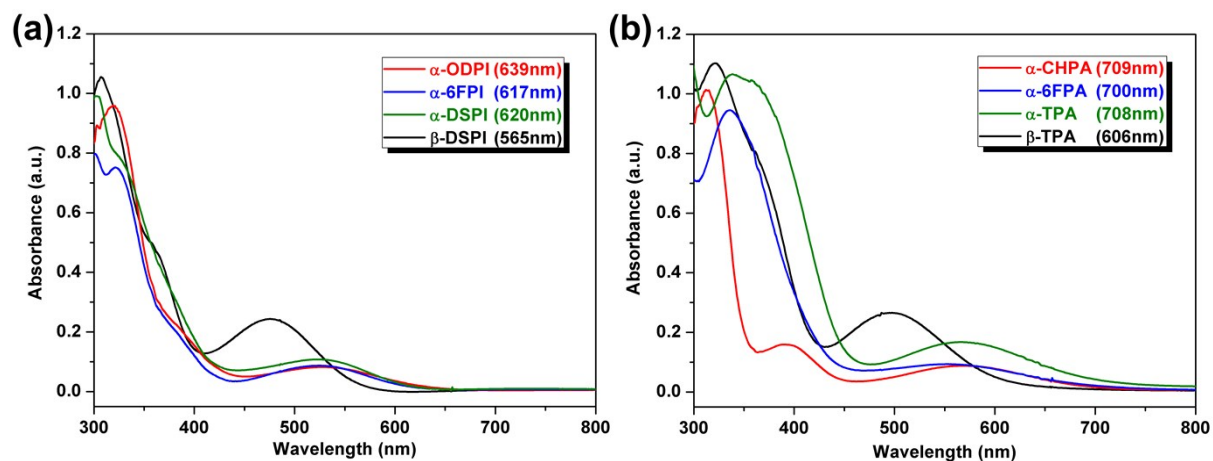


Figure S9. Absorption spectra of (a) polyimide and (b) polyamide thin films. The numbers in the inset show the onset wavelength of each polymer.

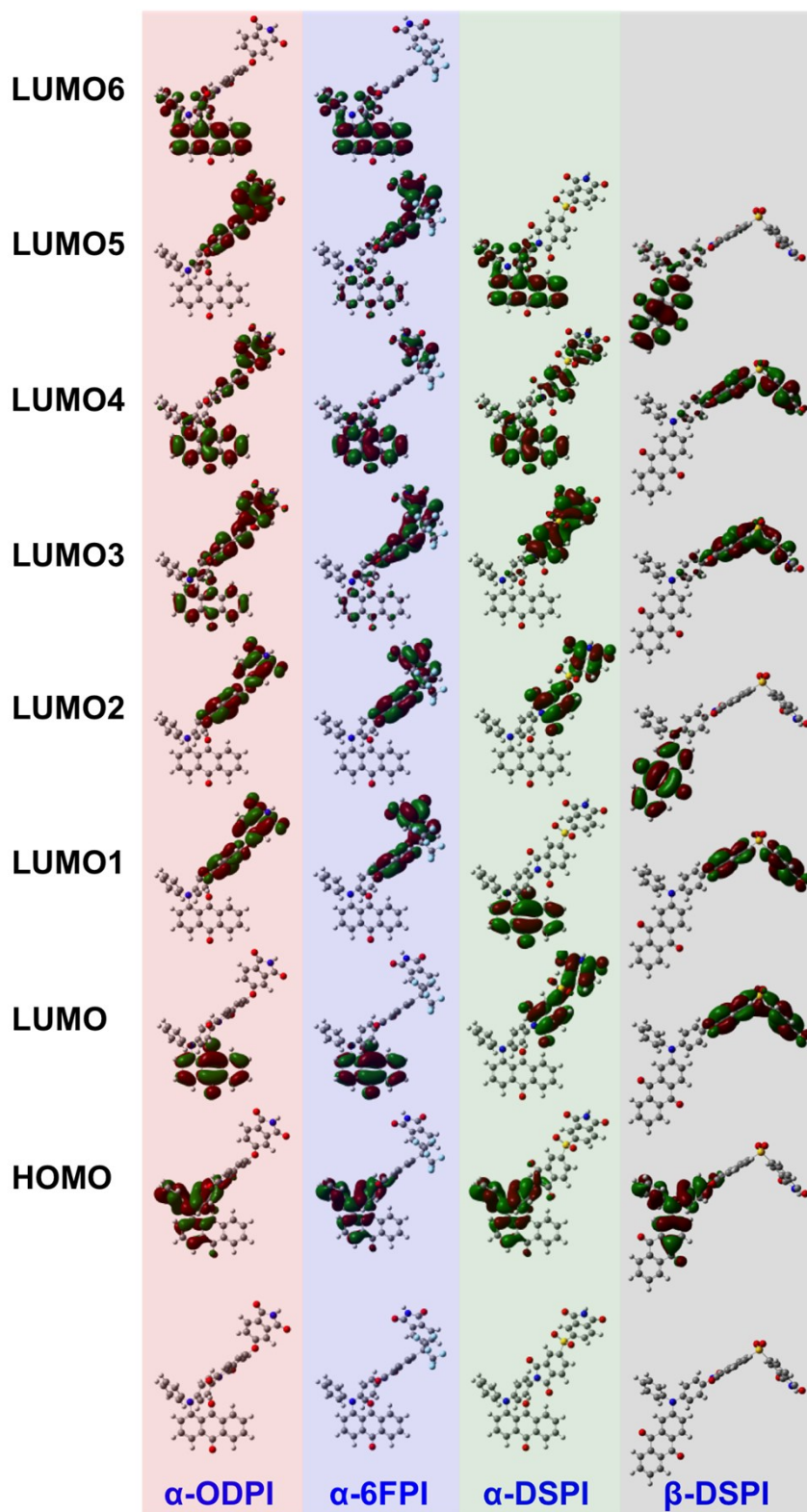


Figure S10. Calculated molecular orbitals and corresponding energy levels of the basic units for the polyimides.

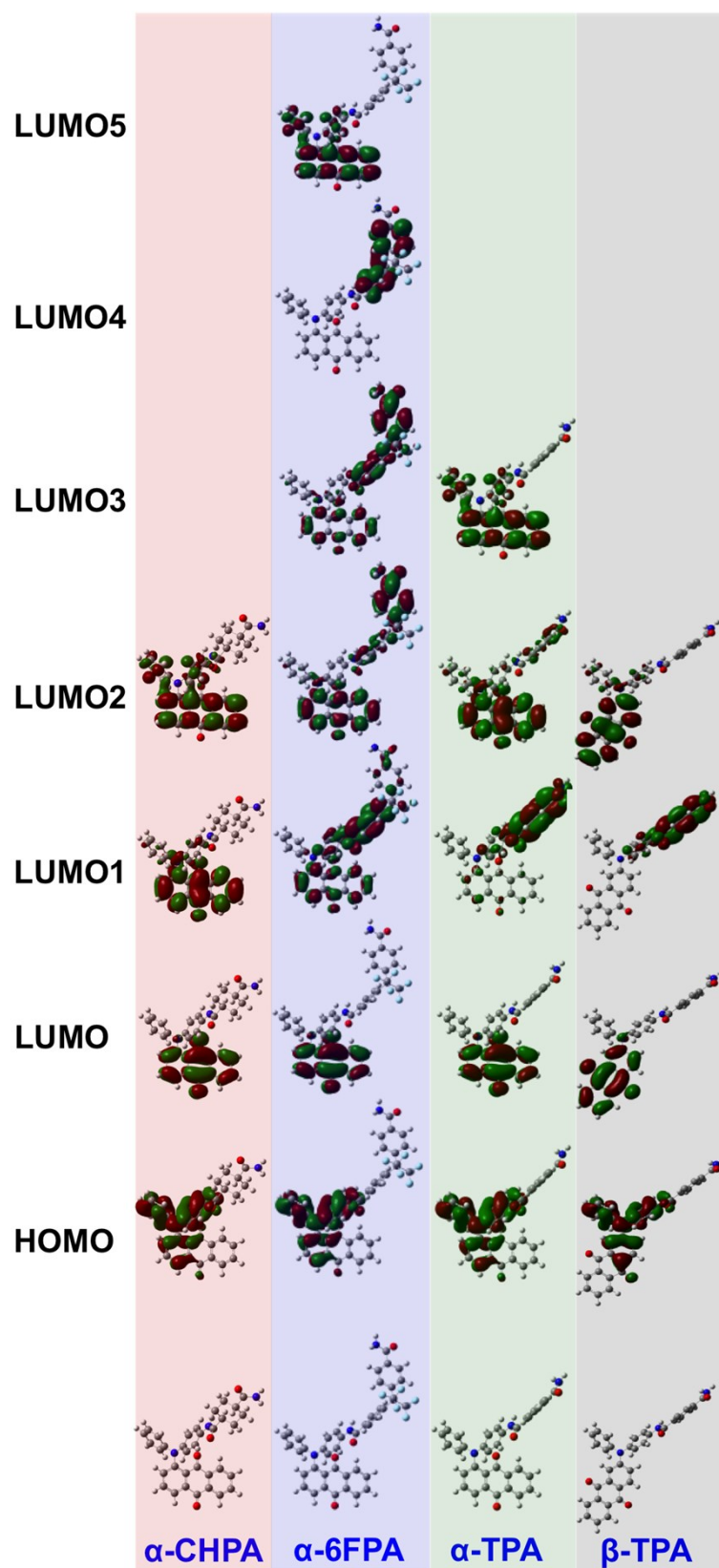


Figure S11. Calculated molecular orbitals and corresponding energy levels of the basic units for the polyamides.

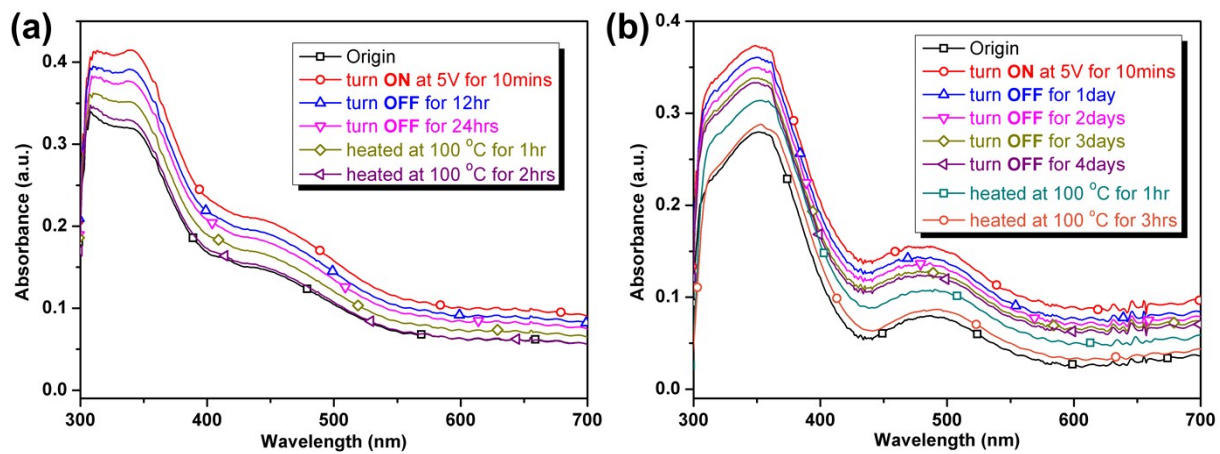


Figure S12. *In situ* UV-visible spectra of the transparent devices of ITO/polymer/ITO: (a) α -6FPI and (b) α -6FPA.

Table S1. Inherent Viscosity and Molecular Weights of Polymers

Code	η_{inh} (dL/g) ^a	M_w ^b	M_n ^b	PDI ^c
α-ODPI	0.35	54,000	29,000	1.86
α-6FPI	0.58	167,000	116,000	1.44
α-DSPI	0.52	209,000	136,000	1.54
β-DSPI	0.56	173,000	154,000	1.12
α-CHPA	0.38 ^d	59,400	29,000	2.05
α-6FPA	0.54 ^d	149,300	56,700	2.63
α-TPA	0.32 ^d	37,700	13,400	2.81
β-TPA	0.30 ^d	27,300	19,300	1.41

^a Measured at a polymer concentration of 0.5 g dL⁻¹ in NMP at 30 °C.

^b Calibrated with polystyrene standards, using NMP as the eluent at a constant flow rate of 0.5 ml/min at 40 °C.

^c Polydispersity Index (M_w/M_n).

^d Measured at a polymer concentration of 0.5 g dL⁻¹ in DMAc at 30 °C.

Table S2. Solubility Behaviors of Polymers

Code	Solubility in various Solvent ^a						
	NMP	DMAc	DMF	DMSO	<i>m</i> -cresol	THF	CHCl ₃
α-ODPI	++	+	—	—	++	++	—
α-6FPI	++	++	++	++	++	++	++
α-DSPI	++	++	+—	+	++	—	—
β-DSPI	++	++	+—	+	++	—	—
α-CHPA	++	++	++	++	+	—	—
α-6FPA	++	++	++	++	+	—	—
α-TPA	++	++	++	++	+	—	—
β-TPA	++	++	++	+	+	—	—

^a Qualitative solubility was tested with 5 mg of a sample in 1 mL of solvent. ++, soluble at room temperature; +, soluble on heating; +—, partially soluble or swelling; —, insoluble even on heating.

Table S3. Thermal Properties of Polymers

Polymer ^a	T_g (°C) ^b	CTE (ppm/K) ^c	T_d at 5 % weight loss (°C) ^d		T_d at 10 % weight loss (°C) ^e		char yield (wt%) ^f
			N ₂	Air	N ₂	Air	
α-ODPI	293	70	510	475	555	520	56
α-6FPI	340	69	515	480	540	520	61
α-DSPI	354	57	480	450	520	470	61
β-DSPI	339	50	520	490	560	525	59
α-CHPA	339	61	400	400	435	435	66
α-6FPA	340	72	465	475	505	510	65
α-TPA	305	53	465	450	510	590	72
β-TPA	312	57	500	480	545	515	66

^a The polymer film samples were heated at 300 °C for 1 h prior to all the thermal analyses.

^b Glass transition temperature measured by TMA with a constant applied load of 5mN at a heating rate of 10 °C/min by film/fiber probe in nitrogen.

^c The CTE data was determined over a 50-200°C range by expansion mode.

^d Temperature at which 5% weight loss recorded by TGA at a heating rate of 20 °C/min and a gas-flow rate of 20 cm³/min.

^e Temperature at which 10% weight loss occurred.

^f Residual weight percentage at 800 °C in nitrogen.